Dispersion-Strengthened Gold

IMPROVED ELECTRICAL CONTACT PROPERTIES

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The improved high temperature properties of dispersion-strengthened gold have been described in an earlier paper in this journal. Now the electrical contact properties of such materials have been investigated and the results are presented. It has been established that these materials can possess the advantageous contact properties of gold without the usual disadvantages, while gold containing a specific amount of cerium oxide has been found to have outstanding contact properties.

Gold and high gold content alloys have a most important property—immunity to the formation of high resistance oxide and sulphide films and organic deposits—which when combined with good electrical conductivity, low hardness and yield point, and low modulus of elasticity, make them excellent materials for the production of electrical contacts. However, the principal disadvantages of gold electrical contacts are too low hardness and low recrystallisation temperature. These cause excessive mechanical wear; high tendency for galling, sticking and welding; and excessive material loss due to arc erosion when used in make and break contacts above low or moderate current values. Electrodeposited hard golds which generally contain 99 to 99.9 per cent gold, with the balance a second metal for hardening, such as nickel, cobalt, silver or cadmium, are used successfully in connectors. Wrought gold alloys are hardened by the addition of other noble metals, for example platinum, palladium or silver, or base metals such as copper or nickel. These alloy additions result in increased hardness which improves the resistance to mechanical wear, and at the same time provides greater resistance to arc erosion as well as sticking and welding.

It should be noted, however, that there are two principal factors which limit the amount of alloying elements that can be added to produce these wrought alloys. The first is that the electrical conductivity decreases rapidly with alloy additions. Many of these alloys have a conductivity in the range of 4 to 12 per cent IACS, compared to 70 per cent for gold, and this limits the current carrying capacity of these materials. The second factor is that alloy additions to gold must be limited in order to retain its outstanding characteristic, its resistance to the formation of oxides and films. Thus noble metals and silver additions are generally limited to about 30 to 40 atomic per cent, and base metal additions equivalent to 14 to 18 carat alloys (58 to 75 weight per cent gold) (1).

To meet the requirements of specific applications, such as sensitive relays, instruments, computers, key switches, slip rings and brushes, radio frequency tuners, and telecommunicative devices, a number of special, high-content gold alloys have been developed to provide the best compromise of contact erosion, welding tendency, and low contact resistance (noise). However, even these special wrought alloys are generally limited to a maximum current value of 0.5 to approximately 2 amperes when long life (10^6 to 10^8 operations) is required. Failure or end-of-life of the gold contacts in these applications is generally reached by one of three mechanisms: (a) formation of a spike and crater erosion pattern, which may lead to bridging the contact gap and result in an interlocking type of weld; (b) actual welding of the contacts, which is considerably enhanced by excessive erosion, or the formation of small molten globules or whiskers on the contact surface and edges; and (c) the development of high and variable contact resistance which results in excessive electrical noise.

It can be seen from the above that the development of improved gold alloys for electrical contacts, especially for higher current values, depends upon the attainment of the following objectives:

(a) increased resistance to arc erosion, in order to minimise the loss or transfer of contact material,

(b) increased resistance to sticking or welding to prevent contact failure,

(c) the retention of low and stable surface contact resistance.

The effect of dispersed oxide phases in increasing the physical properties of precious metals has been extensively investigated, especially for applications

Table I
Composition of Dispersion-Strengthened Gold Alloys

Composition	Oxide Per Cent by Weight†
Au*	
Au+Y_2O_3	0.26
Au+Al_2O_3	0.18
Au+ThO_2	0.20
Au+TiO_2	0.24
Au+CeO_2	0.38

* Control sample of pure gold produced from same gold powder used in the fabrication of dispersion-strengthened alloys
† All approximately 1 volume per cent, except ThO_2 which is about 0.4 volume per cent

at high temperature (2, 3). Dispersion-strengthened gold containing 0.42 per cent by weight (1.85 per cent by volume) of TiO_2 was reported to have substantially improved creep resistance over gold dispersion-strengthened with Al_2O_3 or ThO_2 (4). The hardness of the TiO_2 dispersion-hardened gold in the annealed condition was approximately three times, and the tensile strength was approximately one and one-half times, that of pure gold. The superiority of the tensile strength of the dispersion-hardened gold was increasingly apparent the higher the testing temperature, this ratio becoming 2.5 times at 800°C. Similarly, the 100-hour creep resistance of the dispersion-hardened gold was approximately four times that of gold at 400°C and approximately five times at 500°C.

In a research program carried out at Engelhard Industries Division and supported by the Chamber of Mines of South Africa (5), it was found that the high temperature properties—tensile strength, hardness and stress-rupture—of a number of dispersion-strengthened gold materials were considerably enhanced, without appreciably affecting their electrical properties (resistance, temperature coefficient of resistance and thermal e.m.f.). Although the physical properties of all of the gold materials containing oxide dispersions, approximately 1 volume per cent Y_2O_3, Al_2O_3, TiO_2, and CeO_2 or about 0.4 volume per cent ThO_2, were substantially improved, in the case of high temperature strength the most effective dispersoid was found to be ThO_2 and the second most effective was CeO_2, whereas for wear resistance Al_2O_3 was most effective.

However, since there is little data available in the literature on the effect of these oxide dispersions on the electrical contact characteristics of gold, a considerable portion of our research was then directed towards this end (6). The results of this particular work are summarised in this paper.

Table II
Contact Test Conditions

Parameter	Value
Velocity (cm/s)	2.5
Frequency (Hz)	0.3
Contact Gap (inch)	0.150
Contact Overtravel (inch)	0.070
Make-Force (g)	700
Weld Force (g)	1200 Max.
Contact Bounce	None
Atmosphere	Air
Flow Rate (litres/minute)	1
Voltage, open circuit (volts)	125
Resistance (ohm)	0.4
Arc Current (amperes)	80
Make/Break Arc	Make Only

Preparation of Materials

The gold materials tested for electrical contact properties were those that showed the most effective enhancement of physical and electrical properties, particularly at elevated temperature. The method of preparation of these dispersion-hardened golds, has been covered in the earlier paper (5). These gold materials as well as a sample of pure gold for a control sample were processed to approximately 0.080 inch thick strip. Discs of 3/8 inch diameter were blanked from this strip, and brazed to a standard oxygen-free high conductivity copper rivet to provide test samples for a special contact tester. The brazing was carried out in a 95 per cent nitrogen–5 per cent hydrogen atmosphere using a gold solder. After brazing the composite contact was finish-machined to final diameter and thickness with a 1 inch radius.

The composition of the various gold materials are shown in Table I.

Test Methods

The gold materials were tested in a special type of contact tester. This equipment, originally designed and built by Battelle Memorial Institute, has been expanded and modified by Engelhard to make it suitable to carry out life and performance tests to evaluate the three principal contact characteristics: arc erosion, weld tendency, and contact resistance.

This new contact evaluating equipment is unique and sophisticated. It tests life and performance characteristics of various materials under controlled electrical, mechanical and ambient conditions. It consists of an electro-hydraulic servo-controlled system in which the moving contact is operated

through a bellows system at a varied and controlled cyclic rate, contact gap, and velocity against the stationary contact, which is also supported on a bellows system, and backed up by a temperature controlled dash-pot system. This design provides bounce-free or controlled-bounce operation of the contacts under various conditions.

In the past, one of the basic difficulties in the testing of electrical contacts in research and development studies has always been the problem of translating the laboratory test data to practical and commercial devices. This has led to many different test methods, each designed to evaluate a specific contact characteristic. The new contact tester makes it possible to evaluate the three most important contact characteristics of a material in a single device, under controlled electrical, mechanical, and ambient conditions which simulate the operating conditions of many commercial devices.

In this new equipment the contacts can be tested with D.C. make-arcs, D.C. break-arcs, A.C. make- and break-arcs, or with D.C. current and reversal of polarity. Independent contact opening and closing speeds up to 30 cm/s and contact force up to 1000 g can be used. The effect of make and break arcs on erosion is determined by weight loss of the contacts; the frequency of welding and the actual weld strength is recorded continuously from a transducer system; the contact resistance is measured by a special low-current system at various contact pressures.

Since the primary objective of this test program was to determine the arc erosion and welding characteristics of the dispersion-hardened gold alloys, a high current D.C. make-arc was chosen as the best method of test. Gold and silver alloys are known to produce localised negative transfer under these conditions, and the rate of transfer is proportional to the current and frequency of operation. A high current D.C. make-arc also produces considerable welding. After a number of trials, an arc current of 80 amperes was selected as the best compromise between welding and arc erosion for the accelerated life test. Other test conditions are given in Table II.

Test Results

Arc Erosion

Figure 1 shows the results of the arc erosion tests on the gold and dispersion-hardened gold contact materials, plotted as anode weight loss in milligrams against the number of operations with an 80-ampere make-arc. It can be seen that Al_2O_3, Y_2O_3, TiO_2, and ThO_2, all decreased the amount of erosion (negative material transfer), in that order. However, the effect of CeO_2 was dramatic, since the amount of material loss after 7000 operations was less than one milligram, or less than 0,1 per cent of the original

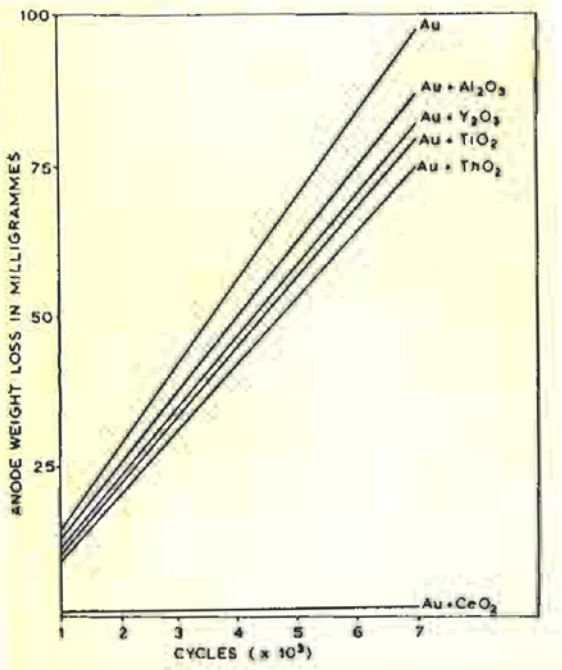

Fig. 1 Arc erosion as a function of cycles of operation for gold and dispersion-strengthened gold electrical contacts with an 80-ampere make-arc

material. Actually, there was a slight anode gain (positive transfer) instead of a loss.

The type and amount of material loss due to arc erosion in the various contacts tested can be seen in the photograph shown in Figure 2. The pure gold contacts (A) show a pronounced cone and crater effect, due to a large amount of negative transfer with this high make-arc current. Gold with a dispersion of ThO_2 (C), Al_2O_3 (D), and Y_2O_3 (E) also shows negative transfer in each case, although the anode weight loss is appreciably less than with pure gold. The

Table III
Anode Loss Due to Arc Erosion After 7000 Operations with an 80-Ampere Make-Arc

Material	Anode Loss (mg)	Anode Loss, Per Cent	Loss Ratio
Au	96.6	5.7	1.00
$Au+Al_2O_3$	85.4	4.9	0.86
$Au+Y_2O_3$	83.0	4.6	0.81
$Au+TiO_2$	78.7	4.5	0.79
$Au+ThO_2$	76.0	4.1	0.72
$Au+CeO_2$	<1. *	<0.05	<0.01

* Anode Gain

Fig. 2 Arc erosion of gold and dispersion-strengthened gold alloys, after 7000 operations, with an 80-ampere make-arc. Upper Contact: Cathode, Lower Contact: Anode

A: Gold B: Gold + CeO_2 C: Gold + ThO_2 D: Gold + Al_2O_3 E: Gold + Y_2O_3

Note the localised negative transfer on Contacts A, C, D, and E compared to the broad diffuse positive transfer on B, gold containing cerium oxide

contact containing a dispersed phase of CeO_2 (B) shows outstanding superiority. Also, these contacts had a broad diffuse type of material transfer instead of localised spikes and craters. This type of transfer is highly desirable, since it makes it possible to use the minimum diameter and thickness of material for maximum economy.

The arc erosion data on these gold alloys are summarised in Table III. The improvement in arc erosion for these various materials over that of pure gold is shown most effectively in the last column, which presents the per cent anode loss for the dispersion-strengthened gold relative to the per cent anode loss for pure gold. For example, gold with Al_2O_3 has 86 per cent erosion and gold with ThO_2 has 72 per cent compared to pure gold. The erosion of gold with CeO_2 is clearly superior, since it is less than 1 per cent of that of pure gold.

Welding Tendency

There is no such thing as a non-welding contact since a weld may occur on each make or break cycle. In this test equipment a force is applied to break the weld, and the weld strength is recorded by the transducer system.

A plot of the per cent of strong and intermediate strength welds, requiring over 100 g to break, that occurred in each interval of 1000 operations, up to a total of 7000 operations, is shown in Figure 3. The alloys with Y_2O_3 and Al_2O_3 showed no appreciable improvement in weld frequency. Gold with ThO_2 and TiO_2 showed substantial improvement in weld

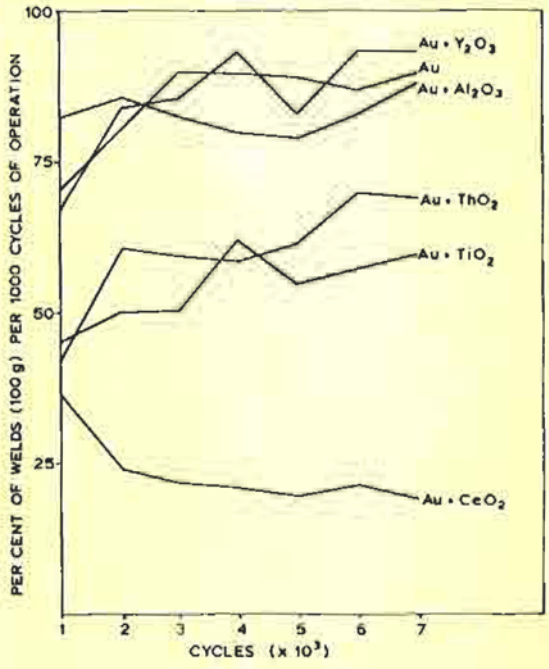

Fig. 3 Per cent of strong and intermediate strength welds (> 100 g) plotted against cycles of operation for gold and dispersion-hardened gold electrical contacts with an 80-ampere make-arc

frequency. Again gold with CeO_2 was outstanding.

The per cent of strong welds, having strengths over 1200 g, which took place with these alloys are given in Figure 4. Gold with Y_2O_3 shows no substantial improvement over pure gold. Al_2O_3, TiO_2, and ThO_2 show some improvement over pure gold. However, gold with CeO_2 is again outstanding.

The weld frequency data are summarised in Table IV. From this it can be seen that gold with Y_2O_3 had no appreciable improvement in strong plus intermediate strength welds or strong welds alone over pure gold; Al_2O_3 had no appreciable affect on strong and intermediate strength welds, but the number of strong welds was about half that of pure gold. ThO_2 and TiO_2 showed considerable improvement, with the strong and intermediate strength welds approximately 70 per cent of that of pure gold, but the strong welds were only about 25 per cent of that of pure gold. Again gold with CeO_2 was outstanding, with only 18 per cent as many strong and intermediate strength welds as pure gold; there was only one strong weld in over 7000 operations, which is less than 0.1 per cent.

Surface Contact Resistance

The results of contact resistance measurements are shown in Table V. The addition of up to 1 per cent by volume of oxides to gold did not have any significant effect on the contact resistance even after 7000 operations, except in the case of CeO_2. This material had a contact resistance about twice the other materials; however, the resistance of approximately 0.2 milliohms after 7000 operations is satisfactory and well below a target of 10 to 50 milliohms; also, this resistance appears to be stable and therefore would not cause excessive noise.

Table IV

Percentage of Strong and Intermediate Strength Welds (>100 g) after 7000 Operations, with an 80-ampere Make-Arc

Material	Total Welds Per Cent	Ratio $\left\{\frac{\text{D.–S. Au}}{\text{Au}}\right\}$
Au	93	1.00
Au+Y_2O_3	93	1.00
Au+Al_2O_3	90	0.97
Au+ThO_2	67	0.72
Au+TiO_2	62	0.67
Au+CeO_2	18	0.19

Percentage of Strong Welds (>1200 g) after 7000 Operations, with an 80-ampere Make-Arc

Material	Strong Welds Per Cent	Ratio $\left\{\frac{\text{D.–S. Au}}{\text{Au}}\right\}$
Au	9.8	1.00
Au+Y_2O_3	9.6	0.98
Au+Al_2O_3	5.4	0.55
Au+TiO_2	3.0	0.31
Au+ThO_2	2.4	0.25
Au+CeO_2	<0.1	0.01

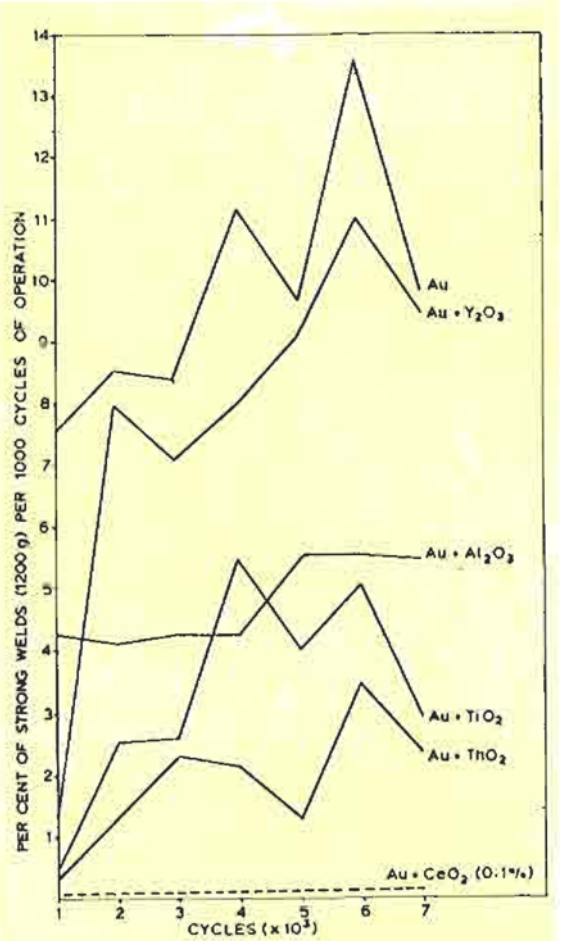

Fig. 4 Per cent of strong welds (>1200 g) as a function of cycles of operation for gold and dispersion-hardened gold electrical contacts with an 80-ampere make-arc

Particle Size

In the present work it was found that the fine particle size and uniform distribution of oxide in these gold alloys was obtained by the thermal decomposition method. The average particle size of the CeO_2 was found to be about 0.6 microns, with occasional particles up to 2.0 to 2.5 microns.

The conventional powder metallurgy technique of admixing metallic and oxide particles and sintering them together does not lead to enhanced physical and

Table V

Contact Resistance of Dispersion-Strengthened Gold Alloy Contacts in Milliohms

Contact Material	Make Force (grams)				Remarks
	300	500	700	1000	
Au	0.14	0.14	0.13	0.11	Original
	0.15	0.12	0.10	0.10	7000 Cycles
	0.14	0.12	0.11	0.09	8800 Cycles
Au+CeO_2	0.17	0.15	0.14	0.12	Original
	0.26	0.24	0.23	0.21	7000 Cycles
	0.24	0.23	0.21	0.19	15,500 Cycles
Au+ThO_2	0.20	0.18	0.18	0.16	Original
	0.10	0.10	0.10	0.08	7000 Cycles
Au+Y_2O_3	0.15	0.15	0.14	0.12	Original
	0.11	0.10	0.10	0.09	7000 Cycles
Au+TiO_2	0.10	0.09	0.09	0.08	Original
	0.08	0.07	0.07	0.07	7000 Cycles

electrical contact properties in the gold dispersion alloys for two principal reasons. The first is that it is difficult to obtain the fine particle size required, and the second is that this method leads to inhomogeneous distribution of the dispersed phase. The internal oxidation method for producing dispersed oxides in gold alloys is not very practical because of the low solubility of oxygen in the matrix.

Discussion and Conclusion

The gold alloy containing 1 volume per cent of CeO_2 had excellent contact properties, with approximately 0.1 per cent of the erosion of pure gold, and only one strong weld in 7000 operations with an 80-ampere make-arc.

It is even more significant to note that this material had a positive material transfer as defined above, that is a slight gain of weight on the anode, with loss of weight on the cathode, as compared to the negative material transfer on pure gold. The alloys containing approximately 1 volume per cent of other oxides had reduced negative transfer compared to gold. It was found also that increasing the oxide content of these alloys above 1 volume per cent caused further decrease in the negative transfer, but did not approach the net "zero" transfer obtained in the 1 per cent of CeO_2. Also, increasing the CeO_2 content above 1 per cent resulted in an increase in the anode gain. Thus the 1 per cent volume of the CeO_2 in this material, together with its fine particle size and uniform distribution, appear to be near optimum for achieving a net "zero" transfer of material.

Excessive material loss, either positive or negative, is undesirable in any contact system. The best contact material is one that shows no appreciable loss on anode or cathode. Since it appears that the amount and direction of material loss can be affected by the amount and nature of the dispersed phase, net "zero" transfer may be achieved in some contact systems by the use of mixed oxides, or by balancing the negative transfer of one material against the positive transfer of a second material. When net "zero" transfer conditions on material transfer are reached, this is always accompanied by improvement in welding properties. Thus the use of dispersed oxides makes it possible to obtain contact materials with improved arc erosion and welding properties.

The degree of strengthening of metals by dispersed oxide phases is related to the diameter and distance between these particles. Recent experience with dispersion hardening indicates that particles considerably smaller than one micron can be obtained, and in most cases finer particles result in a greater increase in hardness and strength. However, there may be a critical particle size and distribution which gives optimum contact properties for different oxides and different matrix metals. The relationship between particle size and the important contact properties of arc erosion and welding in dispersed phase materials has not been fully established.

In summary, these new dispersion-strengthened gold materials have all the advantageous contact properties of gold and high-content gold alloys, that is excellent immunity to corrosion, oxidation, and

organic compounds without having gold's disadvantages of low hardness and strength, and excessive material transfer and welding, especially for higher current values. Gold with CeO_2 has unusually outstanding contact properties, combining high resistance to arc erosion and welding with low and stable contact resistance. These materials can be used wherever gold alloys are now used, such as sensitive relays, key switches, computers, radio frequency tuners, slip rings and brushes, connectors, and telecommunication applications. The superior contact properties of these materials should result in appreciable economic advantages, either by providing improved performance over materials now used by extending the current range or life, or by using less contact material to provide lower cost for comparable performance and life.

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References

1 W. Abbott, *Proc. Holm Seminar*, 1969, 1
2 N. Fuschello and M. L. Gimpl, *J. Mater. Sci.*, 1970, **5**, (12), 1078
3 M. L. Gimpl and N. Fuschello, *J. Mater. Sci.*, 1971, **23**, (6), 39
4 M. Poniatowski and M. Clasing, *Gold Bull.*, 1972, **5**, (2), 34
5 J. S. Hill, *Gold Bull.*, 1976, **9**, (3), 76
6 *U.S. Patent* 4,018,599; 1977

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Gold-Chromium Wire for Pressure Gauges

NEW HEAT TREATMENT IMPROVES STABILITY

The anomalously low temperature coefficient of resistance of gold containing approximately 2 per cent by weight of chromium was first discovered by Linde in 1932 (1), and subsequent studies at the U.S. National Bureau of Standards (2, 3) demonstrated that the alloy should be regarded as a superior corrosion resistant alternative to base metal precision resistance alloys such as Manganin. It now finds considerable application in the measurement of high pressures by the Bridgeman technique, where an essential requirement is that any change in resistance caused by temperature variations should be low compared with the pressure induced increment.

The effect of heat treatment on the temperature and pressure sensitivity of gold-chromium wires has, therefore, received a great deal of attention from the gauge manufacturers, although much of the published information has hitherto been rather confusing. Thus, Darling and Newhall (4) found that the resistance of the gold–2.1 per cent chromium alloy increased linearly with applied pressure within limits as close as 0.25 per cent, was stable after repeated pressure applications, showed no hysteresis, and attained equilibrium after a change in pressure more rapidly than Manganin. Boren, Babb and Scott (5), however, reported that the temperature coefficient of gold-chromium changed with every application of pressure and that the alloy showed considerable hysteresis.

Workers at the Institute of Physics, Warsaw Technical University (6), now appear to have hit upon a method of heat treatment which obviates these disadvantages and brings each individual gauge into a highly stable condition. The complete gauge, wound from hard drawn 0.1 mm diameter wire, is aged at 300°C in a silicone oil bath and the resistance constantly monitored. After an initial slow rise in resistance which peaks after 5 to 6 hours, the resistance then begins to fall, and a broad, fairly stable minimum in the resistance/time curve is attained after 12 to 13 hours at temperature. Gauges which had been brought into this resistance minimum range showed the highest degree of pressure stability and the lowest pressure hysteresis. The resistance/pressure characteristics of such gauges were also linear for all pressures up to 6000 bars. The gauges which showed non-linearity and hysteresis were those whose ageing treatment ended before or after the stable minimum in the resistance/time curve had been attained.

Physical metallurgists will naturally endeavour to correlate these physical and electrical parameters with structural changes within the alloy. The equilibrium solubility of chromium in gold is approximately 8 per cent by weight at 200°C (7), and considerably more at higher temperatures. Evidence of grain boundary precipitation in the 2 per cent chromium alloy has, however, been reported (8), although it seems probable that this would be associated with the presence of impurities. The gold-chromium solid solution begins, however, to order below 325°C (9), and crystallographic details of the Ni_4Mo type superlattice which develops after prolonged annealing have been described by Stolz and Schubert (10). It would therefore be of great interest to relate the pressure stability of the heat treated coil with the degree of ordering which has been introduced.

A. S. D.

References

1 J. O. Linde, *Ann. Physik*, 1932, **15**, (5), 219–248
2 J. L. Thomas, *J. Res., Nat. Bur. Stand.*, 1934, **13**, 681–688 (R. P. 737)
3 T. B. Godfrey, *J. Res., Nat. Bur. Stand.*, 1939, **22**, 565–571, (R. P. 1206)
4 H. E. Darling and D. H. Newhall, *Trans. Am. Soc. Mech. Engrs.*, 1953, **75**, 311
5 M. D. Boren, S. E. Babb and G. J. Scott, *Rev. Sci. Instr.*, 1965, **36**, (10), 1456
6 W. J. Bock and R. Wiśniewski, *Rev. Sci. Instr.*, 1977, **48**, (3), 336
7 E. Raub, *Z. Metallkunde*, 1960, **51**, (5), 290–291
8 L. A. Davies and R. B. Gordon, *Rev. Sci. Instr.*, 1967, **38**, (3), 371
9 E. Watchtel and U. Vetter, *Z. Metallkunde*, 1961, **52**, 525
10 E. Stolz and K. Schubert, *Z. Metallkunde*, 1962, **53**, (7), 433